

L Number	Hits	Search Text	DB	Time stamp
1	1	("5062941").PN.	USPAT; US-PGPUB	2003/07/07 17:13
2	1	("4746369").PN.	USPAT; US-PGPUB	2003/07/07 17:39
3	1	("6238592").PN.	USPAT; US-PGPUB	2003/07/07 17:43
4	1	("6178972").PN.	USPAT; US-PGPUB	2003/07/07 18:18
5	3197	water and (hydrogen adj peroxide) and molybdenum and (etch\$3 or remov\$3)	USPAT; US-PGPUB	2003/07/07 18:23
6	788	(water and (hydrogen adj peroxide) and molybdenum and (etch\$3 or remov\$3)) and ((percentage or percent or ratio or "%") same (hydrogen adj peroxide))	USPAT; US-PGPUB	2003/07/07 18:22
7	633	((water and (hydrogen adj peroxide) and molybdenum and (etch\$3 or remov\$3)) and ((percentage or percent or ratio or "%") same (hydrogen adj peroxide))) and @ad<=20000320	USPAT; US-PGPUB	2003/07/07 18:22
8	146	((water and (hydrogen adj peroxide) and molybdenum and (etch\$3 or remov\$3)) and ((percentage or percent or ratio or "%") same (hydrogen adj peroxide))) and @ad<=20000320) and (molybdenum same (etch\$3 or remov\$3))	USPAT; US-PGPUB	2003/07/07 18:24

United States Patent [19]

Sue

[11] Patent Number: **5,062,941**[45] Date of Patent: **Nov. 5, 1991**

[54] **ELECTROLYTIC PROCESS FOR STRIPPING
A METAL COATING FROM A TITANIUM
BASED METAL SUBSTRATE**

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Conn.**

[21] Appl. No.: **600,929**

[22] Filed: **Oct. 22, 1990**

[51] Int. Cl.⁵ **C25F 5/00**

[52] U.S. Cl. **204/146**

[58] Field of Search **204/146**

[56] **References Cited****U.S. PATENT DOCUMENTS**

3,151,049 9/1964 Hendry 204/146
4,128,463 12/1978 Formanik 204/146
4,356,069 11/1982 Cunningham 204/146
4,404,074 9/1983 Tomaszewski 204/146
4,886,588 12/1989 Curfman 204/146

Primary Examiner—T. M. Tufariello

Attorney, Agent, or Firm—E. Lieberstein

[57] **ABSTRACT**

An electrolytic process for stripping a group IVB or VIB metal coating compound from a titanium based metal substrate using an aqueous electrolyte comprising an oxidizing reagent and an acid with a solution pH of less than 4.5.

7 Claims, No Drawings

ELECTROLYTIC PROCESS FOR STRIPPING A METAL COATING FROM A TITANIUM BASED METAL SUBSTRATE

FIELD OF THE INVENTION

This invention relates to an electrolytic process for selectively stripping a metal coating particularly a compound of a group IVB and VIB metal of the periodic table from a base metal of titanium or an alloy of titanium without chemically attacking the base metal.

BACKGROUND OF INVENTION

High performance components in aircraft engine turbomachines such as compressor blades bearings, gears, impellers and diffusers are typically coated with a metal compound of titanium, zirconium, chromium or tungsten to improve their wear characteristics and to provide erosion protection. The engine parts are cast or otherwise molded or machined from superalloys, stainless steels, alloy steels or titanium alloys and represent very expensive precision components. Removal of the coating from the underlying base metal is necessary if a defect is discovered in the coating and/or for restoring worn components. It is essential to remove the protective coating from the base metal without suffering any detrimental attack to the underlying base metal.

To selectively strip a metal compound of the group IVB and VIB metals of the periodic table inclusive of: titanium, zirconium, hafnium, chromium, molybdenum and tungsten from a titanium alloy base metal is particularly difficult due to the similarity in high corrosion resistance of both the base metal and coating.

Electrochemical stripping of a metal coating from a metal substrate is well known and is basically the reverse of electrodeposition. A reverse current stripping process is disclosed in U.S. Pat. No. 4,356,069 for removing coatings of chromium and nickel from zinc, steel, aluminum, brass or copper using an aqueous solution of chromic acid, peroxide, sulfuric acid and water. A reverse current stripping process is also taught in U.S. Pat. No. 4,128,463 for stripping a coating of a metal carbide such as tungsten carbide from a titanium or titanium alloy substrate. The composition of the electrolyte comprises an aqueous solution of chromic acid or a chromate ion producing material and optionally a sulfate ion added as sulfuric acid. A method for electrolytically stripping a metal containing refractory coating from a base metal using a caustic electrolyte is taught in U.S. Pat. No.'s 3,151,049 and 4,886,588 respectively.

None of the prior art processes are suitable for stripping a metal coating compound of a group IVB and VIB metal such as, for example, a titanium or zirconium compound from a base metal of titanium or a titanium alloy without attacking the base metal or leaving unwanted corrosion pits on the surface of the base metal. The electrolytic process of the present invention is particularly suited for stripping a titanium or zirconium compound or any group IVB or VIB metal compound from a base metal of a titanium metal or alloy without chemically attacking the base metal or forming corrosion pits in the base metal surface.

SUMMARY OF THE INVENTION

The present invention provides a method particularly suited for removal of a compound of a group IVB and VIB metal of the periodic table from a base metal of titanium or an alloy of titanium. According to the pro-

cess of the present invention the base metal is made the anode in an electrolytic cell utilizing as an electrolyte an aqueous solution comprising an oxidizing reagent and an acid at a concentration to provide a solution pH of less than 4.5 and imposing an applied voltage of from about 6 to 40 volts DC at a current density of between 20-700 amperes per square meter over a predetermined time period at a bath temperature of between 50°-70° C. No detrimental attack of the base metal was found to occur and no pitting was observed on the base metal surface.

The concept of the present invention is based upon the use of an oxidizing reagent which causes a reaction with the metal coating compound for forming an oxide with the metal in the metal coating. A layer by layer separation of the newly formed oxide film from the metal coating takes place until the coating is removed without attacking the base metal. The stripping rate is primarily controlled by diffusion of oxygen ions through the coating from the solution. The oxidizing reagent can be any source of oxygen such as air or an oxygen producing compound such as H₂O₂.

DETAILED DESCRIPTION OF THE INVENTION AND EXAMPLES

The present invention relates specifically to an electrolytic process for removing a metal coating from a base metal of titanium or a titanium alloy. Although the process should have applicability to any metal coating which would combine with oxygen for forming an oxide it is particularly suited for use in removing a metal coating of a metal compound of a group IVB and VIB metal of the periodic table inclusive of: titanium, zirconium, hafnium, chromium, molybdenum and tungsten. An example of a titanium compound includes titanium nitride, titanium boride and titanium carbide. A typical example of a titanium alloy base metal is Ti-6Al-4V(AMS4928). Any coating method may be used to form a coating on the base metal.

The configuration of the electrolytic cell is standard and is accordingly not shown. The titanium or titanium alloy base metal is supported or suspended within the aqueous electrolyte solution for forming the anode. The cathode may be any suitable conductor inert to the electrolyte preferably a non-magnetic stainless steel. A DC electrical supply (not shown) is connected from the anode to the cathode to form a direct current circuit through the aqueous electrolyte stripping solution with the applied voltage fixed in a range of between 6 to 40 volts, preferably between 8 to 30 volts at a current density of between 20-700 amperes per square meter.

The aqueous electrolyte comprises a source of oxygen as the oxidizing reagent and an acid in a concentration to adjust to pH of the solution to below 4.5 and preferably between 0.5 and 4.5. The source of oxygen can be air which is fed into the solution at a controlled flow rate to provide a desired volume percent of oxygen in solution or may be supplied from an oxygen producing compound which reacts with water to release oxygen such as hydrogen peroxide or another equivalent peroxide source such as, for example, a perborate, peroxydiphosphate, peroxy sulfate and the like.

Any acid may be added to control the acidity of the solution and at a concentration to maintain a pH of below 4.5. The preferred acid is an organic carboxyl or carboxyl-hydroxyl group acid such as lactic acid, oxalic acid, tartaric acid, formic acid, propionic acid or citric

acid. Alternatively, a diluted inorganic acid may be used such as, for example, acetic acid, nitric acid, HCl or H₂SO₄. The preferred pH range is between .5 to 4.5 and the optimum range in between 1 and 3.5.

The temperature of the electrolyte should be held to between 50°-85° C. and preferably between 50°-70° C.

The following examples substantiate the invention:

EXAMPLE I

Ti-6Al-4V and Ti6Al-2Sn-4Zr-2Mo titanium alloy base metal coupons (1.50×25×50 mm) were coated with a 12 μm TiN coating and immersed in an electrolyte of H₂O-(0.05-0.75) wt.% citric acid-(2.6-4.3) wt.% H₂O₂ in an electrolytic stripping cell. The coated surface of the coupon was surrounded with a cathode ring which was made of electrical conducting material such as stainless steel. Electrical contact from a D.C. powder supply was connected from the coupon as the anode to the cathode ring via alligator clips. The electrolyte had a pH value between 3-3.5 and was agitated and kept at a bath temperature of between 50°-70° C. The power supply was adjusted to provide an electrical potential between 8-25 Vdc across the coupon and the cathode ring. The current density was 20-160 amperes per square meter. After 120 minutes, the coating was completely dissolved into the solution without damage to the underlying base metal of the coupons.

EXAMPLE II

The following table is a compilation of variations in electrolyte, pH and operating conditions using the electrolytic stripping technique as described in Example I for removing a 10 μm ZrN coating from a Ti-6Al-4V compressor blade. The coating was completely removed without any chemical attack to the base metal in one hour.

No.	Electrolyte Composition (wt. %)						Conditions		
	H ₂ O	H ₂ O ₂	Lactic Acid	Oxalic Acid	Citric Acid	Tartaric Acid	pH	Applied Voltage (V)	Current Density (A/m ²)
A	bal.	7.5	6.4	—	—	—	2	25	<240
B	bal.	7.5	—	1.2	—	—	1.5	20	<400
C	bal.	7.5	—	—	2.5	—	2	29	<320
D	bal.	7.5-15	—	—	—	0.5-3.0	0.5-3.5	25	<270

EXAMPLE III

A Ti-6Al-4V coupon (1.50×25×50 mm) coated with a 25 μm thick TiB₂-Ni coating was immersed into the electrolyte consisting of 6% H₂O₂, 1% oxalic acid, and 93% H₂O (in weight percent) with a pH=1.5 at 65° C. for 120 minutes. The stripping set-up was described in Example I. The applied voltage was 6 Vdc and the current density was less than 700 amperes per square meter. The coating was completely removed from the substrate without any damage to it.

EXAMPLE IV

The electrolytic stripping set-up was the same as that in Example I. A solution consisting of water and citric acid up to 10 weight percent with a pH value of 2 was used as an electrolyte. 12 μm TiN and 100 μm WC-Co coated Ti-6Al-4V coupons (1.50×25×50 mm) were immersed into the electrolyte at approximately 60° C.; a N₂-20 vol.% O₂ gas was introduced into the electrolyte via a gas dispersion tube with a flow rate of 0.11m³/hr. and a 15 Vdc electrical potential was applied between

the coated coupon and the cathode ring. The current density was less than 440 amperes per square meter. For approximately 150 and 210 minutes, TiN and WC-Co coatings were removed from the Ti-6Al-4V substrate without any chemical attack to it, respectively.

EXAMPLE V

A TiN coated Ti-6Al-4V impeller was immersed in a solution of 0.3% citric acid, 4.2% H₂O₂ and 95.5% water (in weight percent). The electrolyte had a pH=3 and was kept at 60° C. The coating thickness was approximately 10 μm. A 10 Vdc electrical potential was applied between the impeller and the cathode. After 180 minutes, the coating was completely removed without any chemical attack to the underlying substrate.

EXAMPLE VI

TiN coated Ti-6Al-4 V coupons (1.50×25×50 mm) with a coating thickness of 17 μm were immersed in acid containing electrolytes. An electrical potential of 10-15 Vdc was applied between the cathode and the coated coupon (anode) with a current density up to 320 amperes per square meter at 60° C. Typically, the current density depends on acid concentration, pH value, surface area of the coating, and applied voltage. A N₂-20 vol.% O₂ gas was supplied through a gas dispersion tube with a pore size of 10-15 μm to facilitate the oxidation process of the coating. The gas flow rate was 0.028 cubic meters per hour. After several hours, the coating was completely removed from the substrate without any chemical attack to it. The results are summarized as following:

Electrolytes (wt. %)	Conditions			Total						
	Applied	Current								
Electrolyte Composition (wt. %)										
No.	H ₂ O	H ₂ O ₂	Lactic Acid	Oxalic Acid	Citric Acid	Tartaric Acid	pH	Applied Voltage (V)	Current Density (A/m ²)	Temp. (C.)
A	bal.	7.5	6.4	—	—	—	2	25	<240	65
B	bal.	7.5	—	1.2	—	—	1.5	20	<400	65
C	bal.	7.5	—	—	2.5	—	2	29	<320	65-70
D	bal.	7.5-15	—	—	—	0.5-3.0	0.5-3.5	25	<270	65

H ₂ O	Citric Acid		Oxalic Acid	pH	Voltage (V)	Density (A/m ²)	Stripping time (min)
	1	2					
bal.	1	—	—	2.5	10	<150	240
bal.	0.1	—	—	4.5	15	<80	720
bal.	3	—	—	1.5-2	15	<200	205
bal.	—	2	—	1	10	<320	120

From the above results it can be concluded that a pH value of 4.5 is the highest pH value for practical application.

EXAMPLE VII

A thermal sprayed chromium carbide coating, Cr₃C₂-20 wt. % Nichrome (Nichrome: Ni-20 wt.% Cr) with a coating thickness of 150 μm on a Ti-6Al-4V button (12 mm diameter×2 mm in thickness) was immersed in an electrolyte, consisting of 9 wt. % H₂O₂, 1 wt. % oxalic acid and 90 wt. % H₂O. A 5-10 Vdc electrical potential was applied between the cathode and the coated button at electrolyte temperature of 60°-85° C. The current density varied from 250 to 2200 A/m². After

300 minutes, the coating was completely removed from the metal substrate without deleterious effect on it.

I claim:

1. A method for electrochemically stripping a metal compound of a metal selected from group IVB or VIB of the periodic table from a base metal of titanium or a titanium alloy in an electrolytic cell which comprises the steps of: immersing said base metal having a coating of said group IVB or VIB metal compound thereon into an electrolyte aqueous solution comprising an oxidizing reagent and an acid, said acid having a concentration so as to maintain a solution pH of less than 4.5, connecting said base metal as the anode of said electrolytic cell and a metallic member inert in said aqueous solution as the cathode, imposing a direct current voltage across said anode and cathode in a range of from about 6 to 40 volts DC at a bath temperature of between about 50° C. to 85° C.

2. A method as defined in claim 1 wherein said oxidizing reagent is a source of oxygen.

3. A method as defined in claim 2 wherein said source of oxygen is air fed into said electrolyte at a controlled rate.

4. A method as defined in claim 2 wherein said source of oxygen is an oxygen producing compound which generates oxygen upon contact with water.

5. A method as defined in claim 4 wherein said source of oxygen is selected from the group consisting of hydrogen peroxide, perborate, peroxydiphosphate and peroxysulfate.

6. A method as defined in claims 2 or 5 wherein said acid is an organic acid selected from the carboxyl group or carboxyl-hydroxyl group of acids.

7. A method as defined in claim 6 wherein said solution pH is adjusted between 1 and 3.5.

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**UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION**

PATENT NO. : 5,062,941

DATED : November 5, 1991

INVENTOR(S) : Jiinjen A. Sue

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 1, line 15, after the word "blades", insert --,--.

Column 3, line 49, "Ti-b 6Al-4V" should read "Ti-6Al-4V".

Column 4, line 14, "coaling" should read "coating".

Column 4, line 65, "H₂O" should read "H₂O".

**Signed and Sealed this
Sixth Day of April, 1993**

Attest:

STEPHEN G. KUNIN

Attesting Officer

Acting Commissioner of Patents and Trademarks

United States Patent [19]

Sullivan et al.

[11] Patent Number: 4,746,369

[45] Date of Patent: May 24, 1988

[54] PEROXIDE SELECTIVE STRIPPING COMPOSITIONS AND METHOD

[75] Inventors: Thomas E. Sullivan, Hamden;
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[73] Assignee: Enthone, Incorporated, West Haven,
Conn.

[21] Appl. No.: 18,224

[22] Filed: Feb. 24, 1987

Related U.S. Application Data

[60] Continuation of Ser. No. 776,560, Sep. 16, 1985, abandoned, which is a division of Ser. No. 717,608, Apr. 1, 1985, Pat. No. 4,608,091, which is a continuation of Ser. No. 338,805, Jan. 11, 1982, abandoned.

[51] Int. Cl.⁴ C23G 1/02; C23G 1/02;
C23G 1/00; C11D 7/18
[52] U.S. Cl. 134/3; 134/41;
156/664; 252/99; 252/100
[58] Field of Search 134/3, 41; 156/664;
252/99, 100

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2,876,144 3/1959 Bomberger et al. 134/3
3,367,874 2/1968 Haviland et al. 252/101
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3,953,263 4/1976 Ishikawa et al. 134/3 X
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4,244,833 1/1981 Tomaszewski 156/664 X
4,302,246 11/1981 Brindisi et al. 134/3 X
4,554,049 11/1985 Batenbeck 156/664 X

Primary Examiner—Helen M. S. Sneed

Assistant Examiner—William G. Wright

Attorney, Agent, or Firm—John J. Tomaszewski;

Kenneth A. Koch

[57] ABSTRACT

Acidic stripping solutions comprising hydrogen peroxide as oxidant, either at least one phosphorous-oxy acid, or the addition of nitric acid, together with accelerators and surface active agents, are effective for the rapid and selective removal of protective hard surface coatings and nickel-base brazes from a variety of metal surfaces.

2 Claims, No Drawings

PEROXIDE SELECTIVE STRIPPING COMPOSITIONS AND METHOD

This is a continuation of co-pending application Ser. No. 776,560 filed on Sept. 16, 1985, now abandoned, which application is a divisional of Ser. No. 717,608, filed on Apr. 1, 1985, now U.S. Pat. No. 4,608,091, which application is a continuation of Ser. No. 338,805, filed Jan. 11, 1982, now abandoned.

BACKGROUND OF THE INVENTION

This invention is related to the stripping of nickel-base brazes and "hard surface" coatings from a variety of metal substrates, and, more particularly, to a novel stripping composition and accompanying method for the selective removal of nickel-base brazes and hard surface coatings, applied by plasma spray, detonation gun, sputtering and vapor deposition techniques, to a variety of metal surfaces, without damaging the underlying substrate.

DESCRIPTION OF THE PRIOR ART

Selective metal stripping is one of the most common steps in many industrial manufacturing processes. Usually, the stripping is part of either a general overhaul, involving the refurbishing of a particular coating, or the reclaiming of a defectively plated part. The overhauling process becomes economically feasible when the particular product to be stripped is particularly valuable, such as in the case of high performance aircraft engine components. Also, defective plating will usually occur in a certain percentage of plated parts, resulting from imperfections in the basis metal, improper cleaning, excessive porosity of the substrate which leads to bleeding out of various cleaning and plating solutions, impurities, and human error. The particular method of stripping will usually depend upon the metal (or metals) to be stripped, the substrate material of the basic part, waste disposal requirements, and profitability.

The prior art has employed a variety of both chemical and mechanical methods in an effort to selectively remove protective coatings from the underlying metal substrate, such as the coatings and brazes that are frequently used in the aircraft industry, and particularly in high performance jet engines. Such methods, however, have proven unsatisfactory for a variety of reasons. Low metal stripping rates, general ineffectiveness at low operating temperatures, the handling and disposal of toxic cyanide containing solutions, and the environmental disposal of the spent fluids are problems arising from known chemical methods. Damage to precision machined parts such as jet engine stator assemblies, particularly the large dimensional changes which can result on the metal substrate, as well as pit formation in the base metal caused by pinholes in the hard coating are frequent results of using pressure blasting abrasive tool methods, and electrolytic stripping.

Hydrogen peroxide, H_2O_2 , has been used as an oxidizing agent, in both acid and alkaline solutions, for the selective stripping and etching of metals; however, H_2O_2 has not been effectively adapted for stripping nickel-base metals and "hard surface" coatings, i.e., surfaces which are comprised of intermetallic or cermet compositions, and are applied to the surface to be protected by several high temperature flame deposition techniques, from metal substrates.

Nitric acid, HNO_3 , is a well known stripping agent; however, since it is extremely corrosive it has found infrequent use when selectively stripping, since gentle treatment of the underlying substrate is necessary.

Phosphorous-oxy acids, used herein to signify phosphorous and oxygen containing substances which have a tendency to release a proton in aqueous solution, have found limited usage in the prior art; see, for example, U.S. Pat. Nos. 3,607,398 and 4,128,463; however, they have not been used in combination with peroxide agents nor for selective stripping required during the removal of nickel brazes and hard surface coatings. Selenium compounds and halogen containing accelerators have been used for the stripping of nickel from stainless steel in HNO_3 solutions; however, such solutions also oxidize and corrode the steel substrate.

OBJECTS OF THE INVENTION

Accordingly, it is an object of this invention to formulate an effective composition and accompanying method for the selective stripping of nickel-base brazes and protective hard surface coatings from metal substrates.

It is another object of this invention to formulate a stripping solution which has a much more rapid coating removal rate at lower operating temperatures than those of the prior art.

It is still another object of this invention to formulate a stripping solution for surface coatings which is non-corrosive to the metal substrate.

It is another object of this invention to strip flame sprayed cemented metal carbides, nickel aluminides, nickel graphite and molybdenum from metal substrates used in aircraft engines.

SUMMARY OF THE INVENTION

These and other objects of the invention have been accomplished through the discovery of an aqueous composition useful for the selective stripping of protective hard surface coatings and nickel-base brazes from metals, and particularly high strength alloy substrates, comprising about 75-250 grams/liter (g/l) of a peroxide agent, i.e., usually hydrogen peroxide, about either 50-200 g/l of nitric acid, or in the alternative, about 0-200 g/l of a mixture containing at least one phosphorous-oxy acid, with at least one such acid selected from the group consisting of phosphoric acid, Nitritoltris (methylene phosphonic acid) (NTPA); and hydroxyethane-1,1-diphosphonic acid (HEDPA). Both the nitric and phosphorous-oxy acid peroxide solutions preferably include about 0-40 g/l of an accelerating agent selected from the group consisting of chlorine and bromine containing ions and oxyanions, oxy compounds of Group VI elements such as selenium, and various mixtures thereof; about 0-5 g/l of an inhibiting agent selected from the group consisting of amines, polyamines, amine oxides and mixtures thereof, and about 0-5 g/l of a surfactant, such as a fluorocarbon; the acidity of the stripping solution having a pH value ranging from about -1 to about +0.5. The invention further includes a method for the selective stripping of hard surface coatings and nickel-base brazes from metal substrates, comprising contacting the surface deposit with an aqueous solution of the composition disclosed above, and immersing the surface deposit in the solution until the deposit is substantially removed from the metal substrate without damaging the substrate, keeping the solu-

tion temperature during operation between 20°–55° C., and preferably, about 35°–40° C.

DESCRIPTION OF THE INVENTION

A troublesome problem for the metal stripping art has been to formulate a composition which can selectively strip even the most difficult to remove coatings from metal substrates without damaging the underlying surface to be stripped. The need for such a stripping composition is particularly acute in the aircraft industry, where it is frequently necessary to disassemble and overhaul high performance aircraft engines which contain many expensive, reusable parts, particularly the gas turbine jet engines used, for example, in jet aircraft. The continual development of different protective coatings enabling higher temperature operation has necessitated new approaches to selective stripping. During such an overhaul, there exists a need for a composition which can chemically refurbish these worn or damaged parts, and the removal of brazes and hard surface coatings is an essential step in this process. The stripping agents used for such an overhaul must be very selective, i.e., they must attack only the braze or hard surface coating, while not attacking the underlying expensive metal substrate. Although applicants do not wish to be bound by theory, many of the coatings and brazes currently in use contain quantities of nickel and/or cobalt, and it is believed the dissolution of these metals promotes the loss of structural integrity of the coating or braze. The stripping must also take place at a practical, commercially viable rate, as opposed to just being a laboratory curiosity. The problem is particularly acute when one realizes that based on their chemical composition alone, these coatings may normally be considered more resistant to a chemical attack than the metal substrates they protect, and, in fact, their purpose is to impart high temperature corrosion protection and wear resistance to these metal substrates.

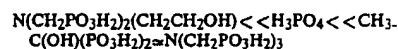
Surprisingly, it has been found that peroxide solutions in combination with either nitric acid, or, in the alternative, a class of mildly aggressive phosphorous-oxy acids, will remove such nickel-base brazes and hard surface coatings, and yet be inhibited from attacking the expensive machined metal substrates. When nitric acid is the acid system of choice, which occurs when high stripping rates are desired, HNO_3 in amounts ranging from about 50–200 grams/liter (g/l), and most preferably, about 75–150 g/l, in combination with a peroxide agent, most preferably H_2O_2 , in amounts of about 75–250 g/l, and preferably incorporating an effective amount of accelerators, inhibitors, and surfactants, gives excellent results. Brazes which can be stripped from metal substrates by such an HNO_3 – H_2O_2 based system include AMS 4779 (94% Ni, 3.5% Si, 1.8% B) from high alloy steel, AMS 4778 (Ni 92, Si 4.5, B 2.9 C 0.06) from AMS 1422, AMS 1424 and AMS 1455 nickel-base alloys, AMS 4777 (Ni 82, Si 4.5 Cr 7.0, B 3.1, Fe 3.0) from 410 Martensitic Stainless Steel (AMS 5504),

and Microbrazed LM (Ni 82.5, Cr 7.0, Si 4.5, B 3.0, Fe 3.0) from Stellite 31 (Co 57, Cr 26, Ni 10, W 7, Carbon 0.5). Hard surface coatings which have been stripped include Metco's 71NS and 71VF alloys (Co 12, C 4, Fe 1, W bal) from 347 and 410 stainless steels, Metco 307 (Ni 75, C 25) from Inconel 600 alloy, and Metco 450 (Al 4.5, Ni Bal) from 4130 steel, Hastelloy X and Inconel 600 substrates.

Surprisingly, it has also been found that peroxide solutions in combination with certain weakly aggressive phosphorous-oxy acids will attack nickel-base brazes and hard surface coatings, and yet be inhibited from attacking the metal substrate. Phosphorous-oxy acids which have been particularly effective are phosphoric acid, nitrilo tris (methylene phosphoric acid) (NTPA), and hydroxyethane-1,1-diphosphonic acid (HEDPA), although most phosphonic acids, as well as many mixtures thereof, are believed to be particularly adaptable to the stripping composition of the invention. The precise amount of the phosphorous-oxy acid depends upon the character of the substrate to be stripped, as well as the coating composition. For example, phosphonic acids NTPA or HEDPA, when mixed with phosphonic acid can range from about 0–200 g/l when stripping from a stainless steel type substrate, and preferably about 100 g/l, while the same acids, when stripping from either titanium base or steel based substrate should be present from about 0–100 g/l and preferably, in about 75 g/l. In the same solution phosphonic and phosphoric acids can range from about 0–200 g/l, and preferably, about 100 g/l.

The greatly preferred peroxide agent of choice is hydrogen peroxide, H_2O_2 , both from the perspective of performance, cost, availability, and environmental effect. But, other peroxide agents, e.g., perborates, peroxydiphosphates, peroxydisulfates and the like, can also be used in place thereof.

In order to maximize stripping effectiveness on steel surfaces, the peroxide and acid concentrations should be balanced. The preferred formulation approach is to combine a major amount of a weakly aggressive phosphorous-oxy acid towards steel and/or titanium with a lesser amount of a more aggressive acid. The order of decreasing acid aggressiveness towards attacking carbon steel in peroxide solution of some commonly available acids of particular interest is as follows:



If the peroxide oxidant concentration becomes exhausted, white or tan salt encrustations begin to form on the attached steel surface, indicating that the steel or titanium has corroded. Hard surface coatings which have been successfully stripped from metal substrates using phosphorous-oxy acid-peroxide-based systems without damaging the substrate can be seen from the following Table:

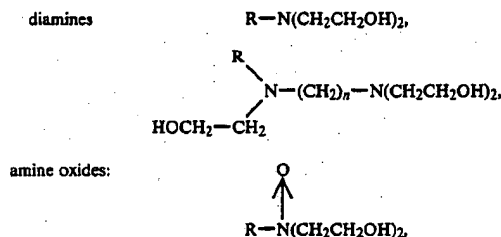
TABLE I
HARD SURFACE COATINGS

Supplier's Trade Name	METCO						UNION CARBIDE						WT-1 WT-2
	63	71 NS	307	450			LM-6A	LW-11B	LW-IN30	LW-IN40			
Coating	Mo	Co 12	Ni 75	Al 4.5			Mo	Wc 88	Wc 87	Wc 85	WC		83
Composition		C 4	C 25	Ni bal				Co 12	Co 13	Co 15	Ti	C	
		Fe 1									Ni 17		

TABLE I-continued
HARD SURFACE COATINGS

Application Method	Plasma Flame Spray				Detonation Gun				
	Stainless Steel	347 S. Steel 410 S. Steel	Inconel 600	4130 Steel Hast-X Inconel 600	Stainless Steel	Titanium 64 alloy	329 S. Steel	Titanium 64 alloy	Steel; Stellite 6 on steel

Amounts ranging from 0-5 g/l of inhibiting agents can significantly aid in preventing chemical attack on the metal substrate particularly in the case of steel and titanium substrates. In particular, those inhibitors selected from the group of alkyl bis (2-hydroxy ethyl)-amines:



where R, represents an alkyl group, and mixtures of each, including different R's for each constituent such as the mixture of aliphatic amines sold under the trade name "Armohib 31", have been found to be effective. However, alky-polyethoxylated amines are ineffective, while mono, di and tri (2-hydroxyethyl) amines have been only marginally effective toward low carbon steels, thus leading to the conclusion that an alkyl group, as well as the 2-hydroxyethyl moiety, is required. It is suspected that the pendant NH_2 groups may provide greater inhibiting qualities than the isoelectronic OH unit. A nonexclusive list of inhibitors includes bis (2-hydroxyethyl) oleyl amine, bis (2-hydroxyethyl) octadecyl amine, bis (2-hydroxyethyl) cocoa amine oxide, bis (2-hydroxyethyl) tallow amine oxide, N,N,N'-tris (2-hydroxyethyl)-N-tallow-1,3-diamine-propane, and imino-bis-propylamine. Although applicants do not wish to be bound by theory, it is believed that a stereochemical characteristic exhibited by these structurally similar compounds is involved in preventing oxidant attack on the substrate. The preferred inhibitor, which is commercially available, sold under the name "Armohib 31" by Armak Chemicals of Chicago, Ill., is an aliphatic amine blend having a proprietary composition.

The addition of Group VI elements, particularly selenium and tellurium containing compounds, and most preferably those selenium compounds such as selenium dioxide, selenous or selenic acids, their metal salts, and mixtures, act to accelerate the removal of the coated deposit. The amounts added should range from about 0-40 g/l, preferably towards the lower end of the range. Halogen containing compounds, particularly such chlorine and bromine ions and oxyanions, such as Cl^- , OCl^- , ClO_3^- , BrO_3^- , I^- , I_2 , IO_3^- , IO_4^- and IO_6^{5-} , as well as their reaction products with peroxide should be effective accelerating agents, particularly when used in conjunction with selenium based accelerating agents. The preferred agents are selenium dioxide

and certain chlorine containing species. Fluorine based ions, however, are not usually as effective as chlorine.

It is further preferred, although not essential, to add small amounts of a surfactant, such as 0-150 mg/l of "DB-31", a silicone based anti-foaming agent sold by Dow Corning Inc., when "Zonyl FSN", a fluorocarbon surfactant marketed by DuPont, or, instead, an amine based compound of the type that are well known in the art is included. These surfactants are desirable because they are resistant to oxidation by the stripping solution, thereby prolonging their life in the bath.

One significant advantage of the stripping composition is that effective stripping can be undertaken at significantly lower operating temperatures than currently required by conventional stripping agents. Stripping can be carried out between 20°-55° C., and preferably, about 35°-40° C., whereas the prior art alkaline solutions operated at a bath temperature of about 60° C. The acidity of the stripping bath is an important parameter for effective stripping; the pH of the acidic stripping solution must remain below about +1, and preferably, below 0, for most effective operation. Thus, most carboxylic acids cannot be used as the acid system since they are not sufficiently acidic, as only strong or moderately strong acids may be employed.

EXAMPLE I

The following composition:

	g/l
Nitrilo tris(methylene phosphonic acid) (NTPA)	82
Phosphoric Acid	62
Hydrogen Peroxide	120
Armohib 31 (Inhibitor)	2.1
DB-31 (non ionic silicone defoamer)	75 mg/l
Water	balance

was warmed to between 22°-57° C. (aver. 35° C.) in order to strip a titanium coupon (AMS 4911) of 7 cm x 4 cm dimension, having a plasma spray coating of 0.3 mm Metco VF-NS, (87WC, 12CO, 1Fe) on one side. The coupon was immersed in the bath for 5 hours, at which time the coating had been stripped from the titanium surface. The coupon was subjected to a load of 300 lb/in² in order to determine whether embrittlement had taken place. No crack formation was observed.

EXAMPLE II

Three titanium shafts coated with a 7-7½ mil coating of LW-11B (WC 88, Co 12) were immersed in the solution of Example I, kept at a bath temperature of 38°-43° C., without any solution agitation, and after three hours the coating had been completely removed without damage to the underlying substrate.

EXAMPLE III

The following solution:

	g/l
Nitrilo tris(methylene phosphonic acid) (NTPA)	82
Phosphoric Acid	30
Hydrogen Peroxide	120
Selenium Dioxide	1
Armohib 31	1
Water	balance

was mixed, and a 2 mil coating of LW-11B (WC 88, Co 12) on a titanium tube was immersed into the solution. The bath was maintained at 25°-35° C., while the tube was frequently agitated during the stripping process. After 1-1½ hours the coating had been stripped, whereupon the machined areas of the part was observed to have retained their original surface finish throughout the entire process.

EXAMPLES IV-V

The following solution:

	g/l
NTPA	82
Hydroxyethane-1,1-diphosphonic acid (HEDPA)	62
Hydrogen Peroxide	120
Armohib 31 (Inhibitor)	2.3
DB-31	75 mg/l
Water	balance

was used to strip WC-Co coatings from both a high alloy steel and a Ti-64 substrate. Both metal coupons were separately immersed in the stripper bath for about five hours, after which time both specimens were removed from the solution. The WC-Co coating had been substantially stripped without damage to either of the underlying substrates.

EXAMPLE VI

The following solution:

	g/l
Nitric Acid	150
Hydrogen Peroxide	150
Selenium Dioxide	0.6
Zonyl FSN	0.29
Water	balance

was mixed, after which a second stage nozzle guide vane, fabricated from Mar-M-200 (1Cb, 9Cr, 10Co, 2Ti, 5Al, 0.14C, 12-5W, 2Hf, bal Ni)+HF (PWA 1422 Directionally Solidified), and having two covers brazed with AMS 4778 (Ni 92, Si 4.5, B 2.9, C 0.06), was immersed for five hours in the solution, which was kept at an average temperature of 40° C. Upon removal from solution, the braze had been completely stripped so the covers could be removed from the vane by gentle prying. No substrate metal attack occurred, but the pack aluminide coating had been partially removed.

EXAMPLE VII

The solution of Example VI was again mixed and used to strip a jet engine part comprising a honeycomb lattice brazed to a high alloy steel with AMS 4779A in

a bath kept at an average temperature of 43° C. After 1½ hours the honeycomb structure separated cleanly from the steel backing.

EXAMPLE VIII

The following solution:

	Volume %
Nitric Acid (70 wt %)	20
Hydrogen Peroxide (50 wt %)	20
Water	balance

was mixed, and an Inconel 600 coupon coated with 25 mils of Metco 307 nickel-graphite was immersed in solution and stripped within ¼ hour at an average bath temperature of 43° C.

EXAMPLE IX

The solution of Example VIII was mixed and an Inconel 600 coupon coated with a 25 mil layer of Metco 450 nickel aluminide was next immersed into the solution, which was kept between 45°-50° C. Complete coating removal required 80 minutes.

EXAMPLE X

The solution of Example VIII was mixed, and a 347 stainless steel shaft coated with a protective covering of 5½ mils of Metco 71 VF (Co 12, Fe 1, WC bal.) was then immersed and stripped in the solution maintained at a temperature between 40°-50° C. After a quarter hour the coating had been completely removed.

EXAMPLE XI

The following solution:

	g/l
Nitric Acid	75
Hydrogen Peroxide	150
Selenium Dioxide	1
Zonyl FSN	0.5
Water	balance

was warmed to between 30°-38° C., whereupon an Inconel X-750 stator segment which had been stripped of its nickel electroplate was immersed in the solution, which was given intermittent agitation during stripping. After 22 hours the AMS 4777 braze had been stripped (1.22 grams), whereupon the outer shroud and foot could be separated from the vane.

EXAMPLE XII

The following solution:

	g/l
Nitric acid	150 g/l
Hydrogen Peroxide	120 g/l
Selenium Dioxide	5 g/l
Zinc Chloride (50 wt %)	8 ml/l
Water	balance

was warmed to 47° C. (over), whereupon a 410 stainless steel "T" section brazed with PWA 996 was immersed for three hours, the solution being subjected to mild mechanical agitation during this time. Upon removal, the braze was sufficiently dissolved to permit separation

of the joined parts. The cut edges of the 410 steel remained shiny and unetched.

EXAMPLE XIII

The following solution:

Nitric acid (50 wt %)	20 vol %
Hydrogen Peroxide (50 wt %)	25 vol %
Aluminum Chloride ($AlCl_3 \cdot 6H_2O$)	23 g/l
Zonyl FSN	0.1 vol %
Water	balance

was warmed to 43° C., whereupon a cobalt base stator assembly fabricated with Microbrazed LM (Ni 82-S, Cr 7, Si 4.5, B 3.0, Fe 3.0) was immersed therein. After 19 hours the braze had been completely selectively stripped allowing separation of the two segments.

Several significant improvements have been realized by these novel compositions. The formulations can strip coatings and brazes from a plurality of metal substrates at stripping rates measured in hours, as compared with days for prior art alkaline solutions. Also, the lower operating temperatures of the solutions of the invention permit the usage of low melting point was maskants. The peroxide reaction products decompose after use to harmless reaction products, H_2O and O_2 , as contrasted with many oxidants in current use which often cannot be easily disposed of, and may pose environmental hazards.

In accordance with the invention, a novel method for stripping hard surface coatings and nickel-base brazes from metal, particularly high strength alloys, has been devised which comprises contacting the surface coating at a temperature of about 30°-45° C., and preferably

about 35° C., with an aqueous solution of the composition described earlier, in an amount sufficient to maintain the acidity, i.e., the pH of the contacting solution at a value between about -1 to 0.5, and continuing the contacting of the surface coating with the solution until the surface coating has been selectively removed from the metal substrate.

During operation, it is preferred that the solution be regularly agitated in order to produce the most efficient stripping conditions. Either workpiece agitation or strong mechanical solution agitation is satisfactory. Spray applications may also be used.

It will be apparent to those skilled in the art that many variations and modifications can be made to the specific embodiments discussed above. All such departures from the foregoing specification are considered to be within the scope of the invention as defined by this specification and the appended claims.

We claim:

1. A method for the selective stripping of tungsten carbide coatings for metal substrates comprising:

- (a) contacting the substrate with an aqueous solution comprising about 75-250 g/l of a peroxide agent, an effective amount of a phosphonic acid and the remainder being water;
- (b) immersing the substrate in the solution at a temperature of about 20°-55° C. until the coating is substantially removed from the substrate; and
- (c) removing the substrate from the solution.

2. The method of claim 1 wherein the phosphonic acid is selected from the group consisting of NTPA, HEDPA and mixtures thereof.

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